DEGRADATION OF EMERGING POLLUTANTS SALICYLIC ACID AND 4-CHLOROPHENOL USING XC-ZnO-CuFe2O4 PHOTOCATALYST

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ABSTRACT

This work focuses on preparing a CuFe2O4/ZnO/Carbon Xerogel (XC) composite designed to be sensitive to sunlight and visible light, with high oxidation and reduction potential. CuFe2O4 was chosen for its valence and conduction bands and its magnetic properties, which aid in separating the photocatalyst from the effluent. Binary materials were characterized using X-ray diffraction. The photocatalytic action of the material was tested on the degradation of emerging pollutants AS and 4CP in a batch reactor. After optimizing synthesis parameters, the photocatalyst was subjected to sono-photocatalysis to enhance degradation. Results indicate that ZnO with 1% CuFe2O4 is more effective in degrading pollutants. Consequently, the synthesis of the ternary material will use this percentage. XC will act as a solid-state mediator to facilitate S-scheme charge transfer in p-n type heterojunctions. Ultimately, the ternary composites will undergo further testing, including diffuse reflectance spectroscopy, scanning and transmission electron microscopy, X-ray diffractometry, infrared and Raman spectroscopy, and N2 absorption-desorption isotherms. In environmental biotechnology, identifying and breaking down emerging micropollutants using advanced oxidative processes has proven to be both promising and essential.

Keywords: Photocatalysis, Zinc oxide, Carbon xerogel, Heterojunction, Ferrite.

1 INTRODUCTION

Advanced oxidative processes (AOPs) are renowned for their strong oxidizing potential and are widely employed in treating effluents containing non-biodegradable pollutants. Among these, heterogeneous photocatalysis emerges as a particularly promising green technology, capable of degrading pollutants into harmless substances like CO2 and H2O[1]. This technology harnesses the energy of light to activate a semiconductor photocatalyst, initiating a series of reactions that lead to the breakdown of complex pollutants. The search for efficient photocatalysts that can operate effectively under visible light is critical for advancing this technology and making it more practical for widespread environmental applications[2]. In environmental biotechnology, the importance of advanced methods for detecting and degrading emerging micropollutants is increasingly recognized. Advanced oxidative processes have emerged as a promising solution to the challenges of environmental pollution. These methods not only efficiently remove and degrade persistent substances but also enhance waste treatment practices in line with environmental conservation and public safety principles[3].

Emerging pollutants, such as salicylic acid and 4-chlorophenol, represent a significant challenge in wastewater treatment due to their persistence and potential adverse effects on ecosystems and human health[4]. These compounds are commonly found in pharmaceutical and industrial effluents and are not effectively removed by conventional treatment processes. As a result, they accumulate in the environment, posing long-term risks. Developing advanced materials and methods for the effective degradation of these pollutants is therefore a priority for environmental scientists and engineers[5]. Photocatalysis offers a potent solution for the degradation of such emerging pollutants. When a semiconductor photocatalyst is exposed to light with energy equal to or greater than its bandgap, electrons are excited from the valence band to the conduction band, leaving behind vacancies in the valence band[6]. These excited electrons and vacancies can participate in redox reactions, generating reactive oxygen species that can degrade pollutants. However, the high recombination rate of these electron-hole pairs in traditional photocatalysts like TiO2 and ZnO limits their efficiency. Enhancing the separation of these pairs and expanding the range of light absorption are key areas of focus to improve photocatalytic performance[7].

To address these challenges, the synthesis of novel semiconductor materials has been explored. One promising approach involves constructing heterojunctions by coupling semiconductors with complementary properties and suitable band positions[8]. This method enhances the separation of photogenerated pairs and increases the absorption of visible light. The use of carbonaceous supports, such as carbon xerogel (XC), further improves the photocatalytic activity due to its stability, specific surface area, and excellent electrical conduction. This project aims to develop ternary XC/ZnO/CuFe2O4 photocatalysts using methods like co-precipitation assisted by ultrasonic induction. These advanced materials are designed to provide efficient degradation of salicylic acid and 4-chlorophenol, leveraging their improved bandgap properties and reduced recombination rates[9].

2 MATERIAL & METHODS

The Preparation of semiconductors, at first, the synthesis of copper ferrite was evidently carried out using the polymeric precursors (PP) method [58]. To this end, in a beaker, 0.1 mol of copper (II) nitrate trihydrate (Cu(NO3)2.3H2O) and 0.2 mol of iron (III) nitrate nonhydrate (Fe(NO3)3.9H2O) were dissolved.) in 50 mL of water. The mixture was left under magnetic stirring. In another beaker,

0.3 mol of citric acid (C6H8O7.H2O) was dissolved. The contents of the first beaker were added to the first one while still stirring. Then, 0.2 mol of ethylene glycol (C2H6O2) was added. In this procedure, the pH was adjusted to maintain it at around 4, with the help of a NaOH base. The semiconductor formed underwent filtration, washing with deionized water and drying in an oven at 100°C until the mass stabilized. Then, the ferrite was calcined at 600 ºC under an N2 atmosphere.

The synthesis of ZnO occurred through the use of a reaction of zinc chloride (ZnCl2) and potassium hydroxide (KOH), simultaneously adding CuFe2O4, with a variation in mass according to the required proportion. In a beaker, 0.06 mol of ZnCl2 were diluted in 50 mL of water. In the same container, while stirring, a solution of 0.12 mol KOH, diluted in 50 mL of water, was inserted. The semiconductor formed also underwent filtration, washing with deionized water and drying in an oven at 100°C until mass constant. The binary materials were calcined at 600ºC. The synthesis of XC/ZnO will be carried out in a similar way to the synthesis of binary materials, differing by the addition of tannin to the ZnCl2 solution. Ternary materials will be calcined at 600 ºC. The CuFe2O4/ZnO mass ratio was varied from 0.01 to 0.1 to evaluate the effect of ferrite content in the materials.

In Characterization, the binary materials were characterized using X-ray diffractometry (XRD). To this end, a PANalytical X'Pert PRO MPD 3060 diffractometer added to copper radiation provided X-ray diffractograms of the binaries.

To assessment of catalyst activity, the tests to determine photocatalytic activity were carried out in 4 jacketed batch reactors. The photocatalyst was added to a solution containing PE (10 mg L−1) and all air was removed from the reaction system, which was kept in the dark until the adsorption-desorption equilibrium was reached. After adsorption-desorption equilibrium, the samples were exposed to irradiation from an artificial light source (Osram ultra-vitalux 300 W lamp for solar irradiation and Osram HNS L 36W 2g11 lamp for UVC irradiation and Osram Powerstar HQI-T 400 W for visible irradiation). PE concentration was analyzed using a UV-Visible spectrophotometer, at characteristic wavelength (224 and 296 nm for 4-CP and AS, respectively)[9,10]. For all analyses, PE aliquots were filtered through 0.22 µm disposable filters and the organic pollutant concentration in the filtrate was determined as mentioned above. All tests were performed in duplicate.

3 RESULTS & DISCUSSION

The X-ray diffractogram of copper ferrite is shown in Figure 3. In the graph in Figure 1, the presence of peaks inherent to the cubic phase of CuFe2O4 can be observed[10].

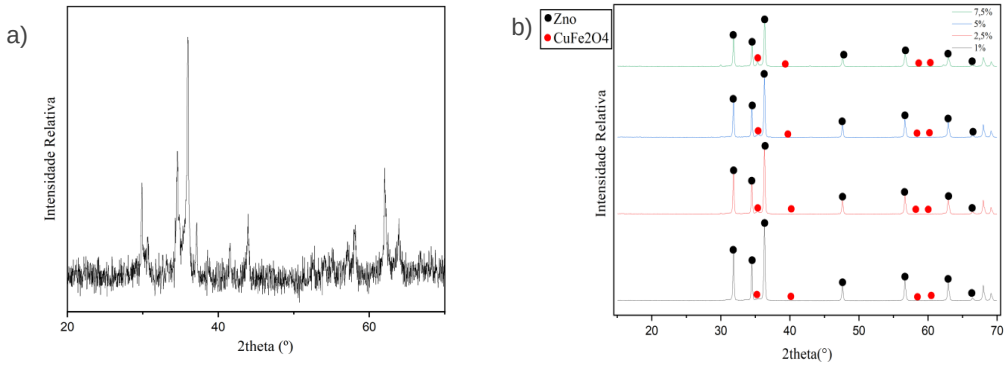

Figure 1 a) DRX graph of pure copper ferrite and b) DRX graph from ZnO Cand uFe2O4.

In addition, a new XRD analysis was carried out using binary materials. In addition to presenting the ferrite peaks (red circles) seen in the previous analysis, the materials demonstrated peaks characteristic of the crystalline structure of zinc oxide (black circles) positioned at[11]: 31.8°, 34.4°, 36.3°, 47.5°, 56.6°, 62.8° and 66.3 Figure 1 b). It is necessary to explain that the evaluation of the results already obtained makes it possible to verify that, based on the literature of[11,12], the desired materials were successfully sintered.

The assessment of photocatalyst degradation, in batch reactors and spectrophotometer, the efficiency of in natura copper ferrite, binary material (composed of zinc oxide, but containing fractions of copper ferrite), zinc oxide and zinc oxide with 0.125g of carbon xerogel was tested. in degrading salicylic acid and 4CP in sunlight. In Figure 3, it is possible to check the percentage of degradation of each material tested depending on the time elapsed by the reaction.

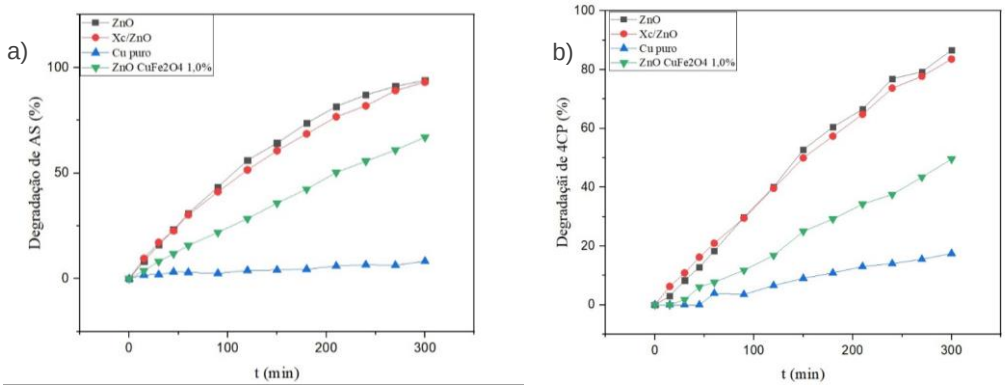

Figure 3: a) AS degradation graph over time and b) 4-CP degradation graph over time

The results indicate that the XC/ZnO composite demonstrates superior photocatalytic performance in degrading salicylic acid (AS) and 4-chlorophenol (4-CP) under sunlight, achieving 93.09% and 83.57% degradation, respectively, after 300 minutes. This enhanced efficiency is attributed to the effective electron-hole separation facilitated by the carbon xerogel (XC), which reduces recombination rates and improves light absorption. Pure ZnO also shows high degradation rates, slightly outperforming XC/ZnO for AS but lagging behind for 4-CP. In contrast, the ZnO/CuFe2O4 (1.0%) composite displays moderate efficiency due to the formation of a heterojunction that aids in electron-hole separation but is not as effective as XC/ZnO.

Pure Cu exhibits the lowest degradation efficiency for both pollutants, highlighting its limitations as a photocatalyst due to high recombination rates and insufficient light absorption. The comparative analysis underscores the importance of developing composite materials like XC/ZnO, which combine efficient charge separation and extended light absorption capabilities, to enhance photocatalytic activity. The promising results with ZnO/CuFe2O4 suggest that further optimization of such heterojunctions could yield better performance, making them viable candidates for advanced photocatalytic applications.

4 CONCLUSION

This work has, as objective, develop new piezo-photocatalysts based on copper ferrite and zinc oxide, for the purpose of de degrade emerging pollutants, for exemple salicilic acid and 4-CP. With the reserch done so far, fit was possible to conclude that the copper ferrite and their binary compounds, like zinc oxide, were synthesized sucessfully, as shown in the DRX analysis. The ideal fraction of copper ferrite for photocatalysis was of 1%, demonstrating piezo-photocatalysts properties under UVC irradiation and ultrassonic.

This study focused on the development of a composite photocatalyst comprising CuFe2O4, ZnO, and carbon xerogel (XC) aimed at enhancing the degradation of emerging pollutants like salicylic acid (AS) and 4-chlorophenol (4-CP). The research successfully synthesized the CuFe2O4/ZnO composite using co-precipitation and optimized the photocatalyst's composition to include 1% CuFe2O4. The characterization results, particularly X-ray diffraction (XRD) analysis, confirmed the successful formation of the intended crystalline structures.

Photocatalytic tests revealed that the XC/ZnO composite achieved superior degradation efficiencies of 93.09% for AS and 83.57% for 4-CP under sunlight, outperforming both pure ZnO and ZnO/CuFe2O4 composites. The enhanced performance of XC/ZnO was attributed to improved electron-hole separation and extended light absorption facilitated by the carbon xerogel. These findings suggest that the incorporation of carbon xerogel and the formation of heterojunctions with CuFe2O4 are promising strategies for developing effective photocatalysts for environmental applications. Future work will involve further optimizing these materials and exploring their performance under various environmental conditions.

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